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[54] BIOCIDAL AZOLYL-PROPANE NITRILES

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514/399; 548/262; 548/341 [58] **Field of Search** 548/341, 262; 514/399, 514/383; 71/92

[56] References Cited

U.S. PATENT DOCUMENTS

4,073,921 2/1978 Miller et al. 548/341 X

FOREIGN PATENT DOCUMENTS

2604047 9/1976 Fed. Rep. of Germany 548/341 3125780 1/1983 Fed. Rep. of Germany 548/341

OTHER PUBLICATIONS

March, J., Advanced Organic Chemistry, McGraw Hill, New York, 1968, pp. 331 and 335.

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[57]

ABSTRACT

Azolyl-propanenitriles are disclosed, of the formula

$$\begin{array}{c|c}
O-R_1 & Y \\
R-C-CH_2-N & \\
CN & N
\end{array}$$

in which

R is an aromatic hydrocarbon or an aromatic hydrocarbon substituted one or more times, the same or differently by halogen, (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, trifluoromethyl, cyano or nitro, R₁ is C₃-C₈ cycloalkyl or C₃-C₈ cycloalkyl substituted by C₁-C₃ alkyl and

Y is N or CH,

and its acid addition salt with an inorganic or an organic acid, as well as processes for the production of these compounds and biocidal compositions containing the same. The compounds display fungicidal activity, growth-regulatory activity, and bactericidal activity.

12 Claims, No Drawings

BIOCIDAL AZOLYL-PROPANE NITRILES

BACKGROUND OF THE INVENTION

The invention concerns new azolyl-propane nitriles, processes for the production of these compounds, as well as biocidal compositions containing the same, and particularly those with fungicidal activity.

PATENT DISCLOSURE STATEMENT

Imidazolyl-propionitrile derivatives with fungicidal activity are already known (DE-OS No. 26 04 047). However, these compounds display a relatively narrow activity spectrum which is unsatisfactory.

Imidazolyl-propionitriles with biocidal activity are likewise already known (DE-OS No. 31 25 780). Despite their fairly good effectiveness, there remains a need for compounds with still better characteristics.

OBJECT AND SUMMARY OF THE INVENTION 20

It is therefore an object according to the present invention to develop new propionitrile derivatives which open up broadly multiplied use possibilities, particularly in the field of plant protection, and which provide greater fungicidal activity.

This object is obtained according to the present invention by azolyl-propane nitriles of the general formula

in which

R is an aromatic hydrocarbon or an aromatic hydrocarbon substituted at least once by the same or by different (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, trifluoromethyl, cyano or nitro R₁ is C₃-C₈-cycloalkyl or 40 C₃-C₈-cycloalkyl substituted by C₁-C₃-alkyl radicals and

Y is N or CH,

and their acid addition salts with inorganic or organic acid.

The compounds according to the present invention are in the broadest sense biocidally effective. They are characterized however, in particular by a fungicidal activity which, in a surprising manner, exceeds that of known active substances of analogous constitution and 50 activity.

The fungicidal activity, surprisingly, is effective against fungi having the most different systematic structures. Used in treatment of above-ground plant parts, they protect against wind borne pathogens. The compounds also can be employed for the treatment of seed goods against seed-transportable pathogens. Moreover, they work systematically, that is, they are withdrawn by the roots of the plants, for example, after application during the sowing, and are then transported into the 60 above-ground parts of the plants to protect the same against pathogens.

As further activities characteristic of the compounds according to the present invention, mention may be made of their growth-regulatory and bactericidal activities.

Because of their broad activity spectrum, the compounds according to the present invention are suitable

not only for the protection of so-called culture plants but also for the protection of materials and for the control of human pathogenic and animal pathogenic microbes, and therefore exhibit broadly multiplied use possibilities. Depending upon the presence of specific substituents, the compounds according to the present invention display various outstanding activity. Thus, the compounds can be employed as fungicides, and plant-growth regulators. The compounds according to the present invention also find use as plant-growth regulators which are characterized, for example, by the following use possibilities:

Reduction in the vegetative growth of woody and weed plants, for example, at road borders, railroad plants and the like, in order to prevent too abundant a growth. Reduction in growth grain in order to prevent depositing or breaking-off; and with cotton, in order to increase the yield.

Influencing the branching of vegetative and generative organs with ornamental or culture plants, in order to multiply the onset of blooming; or with tobacco and tomato in order to reduce the development of sideshoots.

Improvement of the fruit quality, for example, increasing the sugar content of sugar beets, sugar cane or fruit; and a more uniform ripening of the harvest goods, which leads to higher yields.

Increasing the resistance against climatic influences such as cold and dryness.

Influencing the latex flow of rubber plants.

Formation of parthenocarpic fruit, pollen sterility and sexual influence are likewise possibilities of use.

Control of the germination of seeds or the driving out of buds.

Defoliation or influencing the fruit fall in order to facilitate harvesting.

The compounds according to the present invention are suitable in particular for influencing the growth of beta beets. They also display desirable growth-regulatory effects with grain, soybeans and cotton.

The amounts of active compounds, depending upon specific use applied, range generally from 0.05 up to 5 kg of active substance per hectare. However, if necessary even higher application amounts can be employed.

The time of employment depends upon purpose of use and the climatic conditions.

In the compounds of general formula I, the substituents can represent, for example:

R is 2-fluorophenyl, 3-fluorophenyl, 4-fluorophenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 2-3-bromophenyl, bromophenyl, 4-bromophenyl, 2-3-iodophenyl, iodophenyl, 4-iodophenyl dichlorophenyl, 3,4-dichlorophenyl, 2,6-dichlorophenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2-ethylphenyl, 3-ethylphenyl, 4-ethylphenyl, 2-propyl-3-propylphenyl, 4-propylphenyl phenyl, propyphenyl, 3-isopropylphenyl, 4-isopropylphenyl, 2-butylphenyl, 3-butylphenyl, 4-butylphenyl, 2-secbutylphenyl, 3-sec-butylphenyl, 4-sec-butylphenyl, 2tert-butylphenyl, 3-tert-butylphenyl, 4-tert-butylphenyl, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, 2-ethoxyphenyl, 3-ethoxyphenyl, 4-ethoxyphenyl, 2-methylthiophenyl, 3-methylthiophenyl, 4methylthiophenyl, 2-ethylthiophenyl, 3-ethylthiophenyl, 4-ethylthiophenyl 2-trifluromethylphenyl, 3-trifluormethylphenyl, 4-trifluromethylphenyl, 2-nitrophenyl, 3-nitrophenyl, 4-nitrophenyl, 3-fluoro-4-methox-

yphenyl, 3,4,5-trimethoxyphenyl, 5-chloro-2-nitrophenyl, 3-chloro-5-nitro phenyl or 4-chloro-2-fluorophenyl

R₁ can be cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, 2-methylcyclopentyl, 2-methylcyclohexyl, 2,2-dimethylcyclopentyl, or 5 2,2-dimethylcyclohexyl and

Y is N or CH.

Not only inorganic acids but organic acids can be used to form the acid addition salts. These include the following:

hydrochloric acid and hydrobromic acid, phosphoric acid, sulfuric acid, particularly nitric acid, mono- and bi-functional carboxylic acid and hydroxycarboxylic acids, such as, for example, acetic acid, maleic acid, succinic acid, furmaric acid, tartaric acid, citric acid, 15 salicylic acid, sorbic acid, lactic acid, as well as sulfonic acids such as for example, p-toluene sulfonic acid and 1,5-naphthalene disulfonic acid.

The acid addition salts can be formed by customary salt formation techniques, for example, by dissolving a 20 compound of formula I in a suitable solvent and then adding the acid.

An outstanding fungicidal activity is displayed for example, by the following compounds:

2-(4-chlorophenyl)-2-cyclopentyloxy-3-(imidazol-1-25 yl)-propanenitrile and the hydronitrate; 2-(4-chlorophenyl)-2-cyclopentyloxy-3-(1,2,4-triazol-1-yl)propanenitrile and the hydronitrate; 2-cyclopentyloxy-3-(imidazol-1-yl)-2-(2-methylphenyl)-propanenitrile and the hydronitrate; 2-cyclopentyloxy-2-phenyl-3-30 (1,2,4-triazol-1-yl)-propanenitrile, and the hydronitrate; 2-(2-chlorophenyl)-2-cyclopentyloxy-3-(1,2,4-triazol-1yl)-propane-nitrile and the hydronitrate; 2-cyclopentyloxy-3-(imidazol-1-yl)-2-phenyl-propanenitrile, the hydronitrate.

Aside from the above-designated activities, the compounds according to the present invention also are bactericidal which allows further possibilities of employment.

The compounds according to the present invention 40 can be used either alone or in mixture with one another or with other active substances. If necessary, other plant-protection or pest-control agents can be added, according to the desired purpose.

The active substances of the invention or their mix- 45 tures are employed in the form of preparation such as powders, spray agents, granulates, solutions, emulsions or suspensions, with the addition of liquid and/or solid carrier material, respectively, diluting agents and, if necessary, wetting, adhering, emulsifying and/or dis- 50 persing adjuvants.

Suitable liquid carrier substances include, for example, water, aliphatic and aromatic hydrocarbons, such as benzene, toluene, xylene, cyclohexanone, isophorone, dimethylsulfoxide, dimethylformamide, more- 55 over, mineral oil fractions and plant oils.

Suitable as solid carrier materials are mineral earths, for example tonsil, silica gel, talcum, kaolin, attapulgite, limestone, silicic acid and plant products, for example, meal.

Examples of surface-active substances include: calcium lignin sulfonate and their salts, formaldehyde condensate, fatty alcohol sulfate, as well as substituted benzene sulfonic acids and their salts.

Insofar as the active substances are supposed to be 65 employed for disinfection of seed goods, dyes can be admixed in order to provide the pickledseed goods with a clearly visible coloration.

The portion of the active substance in the various preparations can range within broad limits. For example, the composition can contain from about 10 to 90 percent by weight active substance, about 90 to 10 percent weight liquid or solid carrier material, as well as, if necessary, up to 20 percent by weight of surface-active substance, upon corresponding reduction in the amount of carrier.

The present composition can be applied in known manner, for example, with water as the carrier in spray amounts of about 100 up to about 10,000 liter/ha. The compositions also can be used in the so-called lowvolume or ultra-low-volume techniques, and in the form of microgranulates.

By way of non-limiting examples, the following typify the compounds of the invention.

A. Spray Powder

(a) 40 percent by weight active substance

25 percent by weight clay mineral

20 percent by weight silicic acid

10 percent by weight cell pitch

5 percent by weight surface-active substance based upon a mixture of the calcium salt of lignin sulfonic acid, alkylphenolpolyglycolether

(b) 20 percent by weight active substance

60 percent by weight kaolin

15 percent by weight silicic acid

5 percent by weight surface-active substance based upon the sodium salt of N-methyl-N-oleyltaurine and the calcium salt of lignin sulfonic acid

(c)

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10 percent by weight active substance

60 percent by weight clay minerals

15 percent by weight silicic acid

10 percent by weight cell pitch

5 percent by weight surface-active substance based upon the sodium salt of N-methyl-N-oleyltaurine and the calcium salt of lignin sulfonic acid

B. Paste

45 percent by weight active substance

5 percent by weight sodium aluminum silicate

15 percent by weight cetylpolyglycolether with 8 mol ethylenoxide

2 percent by weight spindle oil

10 percent by weight polyethyleneglycol

23 parts water

C. Emulsion Concentrate

25 percent by weight active substance

15 percent by weight cyclohexanol

55 percent by weight xylene

5 percent by weight mixture of nonylphenylpolyoxyethylene or calcium dodecylbenzene sulfonate

The new compounds according to the present invention can be produced by reacting compounds of the general formula

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or their alkali salts in the presence of a solvent and, if necessary, in the presence of a base, whereby R, R₁ and Y have the above given meaning, and X is halogen, alkylsulfonyloxy or arylsulfonyloxy, or alkylsulfonyloxy or arylsulfonyloxy halogenated in a side chain.

Examples of halogen include chlorine, bromine or iodine; methyl, ethyl, propyl and trifluoromethylsulfonyl are suitable as alkylsulfonyloxy; whereas examples 15 of arylsulfonyloxy include benzene sulfonyloxy and p-toluene sulfonyloxy.

When a solvent is employed it is desirable to select a material which is inert with respect to the reactants, preferably polar, aprotic substances such as N,N-dimethylformamide, N-methylpyrrolidone, tetramethylurea, hexamethylphosphoric acid triamide and dimethylsulfoxide, and even higher boiling aromatic and aliphatic hydrocarbons such as toluene, fluorobenzene, or xylene. The reaction temperature can be varied within 25 broad limits. Preferably a temperature between 100° C. and 200° C. is used. The reactions follow under normal or excess pressure.

The novel features which are considered as characteristics of the invention are set forth in particular in the 30 appended claims. The invention itself, however, both as to its construction and its method of operation, together with additional objects and advantages thereof, will be best understood from the following description of specific embodiments.

DESCRIPTION OF PREFERRED **EMBODIMENTS**

Example 1

2-cyclopentyloxy-3-(imidazol-1-yl)-2-(methylphenyl)propanenitrile, hydronitrate

60.7 g (0.188 mol) 2-cyclopentyloxy-2-(2-methylphenyl)-3-methylsulfonyloxy-propanenitrile, 63.9 g (0.938 mol) imidazole and 3.88 ml DMF are stirred for 45 six hours at 160° C. bath temperature. They are then poured into 200 ml water, extracted twice—each time with 200 ml methylene chloride—and the organic phase is then dried with MgSO₄. It is then rotated in a vacuum after which the oil is dissolved in 100 ml isopropanol 50 and then reacted dropwise with 10 ml 100% nitric acid, with cooling with ice. Next follows 20 minutes afterstirring with RT, addition of 200 ml acetic ester, and evacuation in a vacuum. In this manner 30.7 g of the title compound are obtained, MP: 160° C. (decomposi- 55 tion).

Example 2

2-cyclopentyloxy-3-(imidazol-1-yl)-2-(methylphenyl)propanenitrile

28.5 g of the hydronitrate obtained in Example 1 are dissolved in 300 ml methanol. Within a period of 5 minutes and at a temperature of between 5° and 15° C., 100 ml dilute ammonia solution are added dropwise. The mixture is then diluted with 750 ml water and ex- 65 tracted twice, each time with 300 ml ethyl acetate. Then follows drying with MgSO₄, centrifuging to dryness, and reaction of the remaining oil with 200 ml hexane,

whereafter crystallization occurs. In this manner are obtained 21.7 g of the title compound, MP: 92° C.

Example 3

2-cyclohexyloxy-2-(2-methylphenyl)-3-(1,2,4-triazol-1yl)-propanenitrile, hydronitrate

9.8 g of 1,2,4-triazol are heated in a mixture of 120 ml dimethylsulfoxide and 70 ml xylene with 5.7 g NaOHtablets for two hours at 180° C. bath temperature. Reaction water is removed in a water separator. The bath temperature is then allowed to drop to 150° C., and 32 of 2-cyclohexyloxy-3-methansulfonyl-2-(2-methylphenyl)-propanenitrile and a little DMSO are added to the reaction mixture. After stirring for three hours at 150° C., ice-water is aded, followed by two extractions, each time with 200 ml methylene chloride, whereupon the organic phase is washed again with 100 ml H₂O. Then follows drying with MgSO₄, spinning, take up in 70 ml isopropanol and dropwise reaction under ice cooling with 3.9 ml. 100% nitric acid. The reaction mixture is then reacted with 50 ml ether, evacuated in a vacuum and then recrystallized from isopropanol. 14.36 g of the title compound are obtained, with melting point 194°-197° C. (decomposition).

In analogous manner, using appropriate starting materials the following compounds according to the present invention are prepared:

Ex-		
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ple	Name of Compound	Physical Constant
4	2-cyclopentyloxy-2-(2-methyl-	MP: 142-144° C. (D)
	phenyl)-3-(1,2,4-triazol-1-yl)-	
	propanenitrile, hydeonitrate	•
5	2-cyclohexyloxy-3-(imidazol-1-	MP: 150-152° C. (D)
	yl)-2-(2-methylphenyl)-propane-	· · · · · ()
	nitrile, hydronitrate	
6	2-cyclohexyloxy-3-(imidazol-1-	MP: 114-116° C.
	yl)-2-(2-methylphenyl)-propane-	
	nitrile	
7	2-cyclohexyloxy-2-(2-methyl-	MP: 82-85° C.
	phenyl)-3-(1,2,4-triazol-1-yl)-	
	propanenitrile	
8	2-cyclohexyloxy-3-(imidazol-1-	MP: 75° C.
	yl)-2-phenyl-propanenitrile	
9	2-cyclohexyloxy-3-(imidazol-1-	MP: 211-212° C. (D)
	yl)-2-phenyl-propanenitrile,	
	hydronitrate	
10	2-(2-chlorophenyl)-2-cyclohexyl-	MP: 128° C.
	oxy-3-(imidazol-1-yl)-propane-	•
	nitrile	
11	2-(2-chlorophenyl)-2-cyclohexyl-	MP: 186–188° C. (D)
	oxy-3-(imidazol-1-yl)-propane-	
10	nitrile, hydronitrate	3.55 0.4 0.50
12	2-cyclohexyloxy-2-phenyl-3-	MP: 94-97° C.
	(1,2,4-triazol-1-yl)-propane-	
13	nitrile	MD 105 1068 (C. (D.)
13	2-cyclohexyloxy-2-phenyl-3-	MP: 185–186° C. (D)
	(1,2,4-triazol-1-yl)-propane- nitrile, hydronitrate	•
14	2-(4-chlorophenyl)-2-cyclohexyl-	MD. 214 215° C (D)
• '	oxy-3-(imidazol-1-yl)-propane-	MP: 214–215° C. (D)
	nitrile, hydronitrate	
15	2-(2-chlorophenyl)-2-cyclohexyl-	MP: 109-112° C.
	oxy-3-(1,2,4-triazol-1-yl)-propane-	
	nitrile	
16	2-(2-chlorophenyl)-2-cyclohexyl-	MP: 139° C. (D)
	oxy-3-(1,2,4-triazol-1-yl)-propane-	1411 · 157 C. (13)
	nitrile, hydronitrate	•
17	2-cyclopentyloxy-3-(imidazol-1-	n_D^{20} : 1.5462
· -	yl)-2-phenyl-propanenitrile	
18	2-cyclopentyloxy-3-(imidazol-1-	MP: 164-167° C. (D)
	yl)-2-phenyl-propanenitrile,	
	hydronitrate	

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COMMINICAL	

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Ex-		
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ple	Name of Compound	Physical Constant
19	2-(2-chlorophenyl)-2-cyclopentyl-	n_D^{20} : 1.5590
• /	oxy-3-(imidazol-1-yl)-propane-	II <i>D</i> ==: 1.3390
	nitrile	
20	2-(2-chlorophenyl)-2-cyclopentyl-	MD: 120° C (D)
20	oxy-3-imidazol-1-yl)-propane-	MP: 130° C. (D)
	nitrile, hydronitrate	
21	2-cyclopentyloxy-2-phenyl-3-	MP: 85-88° C.
21	(1,2,4-triazol-1-yl)-propane-	MIF: 03-00 C.
	nitrile	
22	2-cyclopentyloxy-2-phenyl-3-	MP: 172-174° C.
	(1,2,4-triazol-1-yl)-propane-	MIP: 1/2-1/4 C.
	nitrile, hydronitrate	
23	2-(2-chlorophenyl)-2-cyclopentyl-	MP: 91-94° C.
23	oxy-3-(1,2,4-triazol-1-yl)-propane-	MII: 71-74 C.
	nitrile	
24	2-(2-chlorophenyl)-2-cyclopentyl-	MP: 136° C. (D)
	oxy-3-(1,2,4-triazol-1-yl)-propane-	MII. 130 C. (D)
	nitrile, hydronitrate	
25	2-cyclohexyloxy-2-(2,4-dichloro-	n_D^{20} : 1.5565
	phenyl)-3-(imidazol-1-yl)-	пр . 1.5505
	propanenitrile	_
26	2-cyclohexyloxy-2-(2,4-dichloro-	MP: 156° C. (D)
	phenyl)-3-(imidazol-1-yl)-	1.11 . 150 C. (D)
	propanenitrile, hydronitrate	
27	2-(4-chlorophenyl)-2-cyclohexyl-	MP: 97° C. (D)
	oxy-3-(1,2,4-triazol-1-yl)-	1,11 .) , (1)
	propanenitrile	
28	2-(4-chlorophenyl)-2-cyclohexyl-	MP: 176-178° C. (D)
	oxy-3-(1,2,4-triazol-1-yl)-	
	propanenitrile, hydronitrate	
29	2-cyclohexyloxy-2-(2,4-dichloro-	MP: 121-124° C.
	phenyl)-3-(1,2,4-triazol-1-yl)-	
	propanenitrile	
30	2-cyclohexyloxy-2-(2,4-dichloro-	MP: 145-148° C. (D)
	phenyl)-3-(1,2,4-triazol-1-yl)-	
	propanenitrile, hydronitrate	
31	2-(4-chlorophenyl)-2-cyclopentyl-	MP: 100-102° C.
	oxy-3-(imidazol-1-yl)-propane-	
20	nitrile	
32	2-(4-chlorophenyl)-2-cyclopentyl-	MP: 200–201° C. (D)
	oxy-3-(imidazol-1-yl)propane-	
22	nitrile, hydronitrate	1.6TD 00 000 0
33	2-(4-chlorophenyl)-2-cyclopentyl-	MP: 89–92° C.
	oxy-3-(1,2,4-triazol-1-yl)-	
34	propanenitrile	MD 160 1669 G (D)
34	2-(4-chlorophenyl)-2-cyclopentyl-	MP: 162-165° C. (D)
	oxy-3-(1,2,4-triazol-1-yl)-	
35	propanenitrile, hydronitrate	20. 1.5220
33	2-cyclopentyloxy-2-(2-fluorophenyl)- 3-(imidazol-1-yl)-propanenitrile	nD=0: 1.5528
36	2-cyclopentyloxy-2-(2-fluorophenyl)-	MD. 60 62° C
50	3-(1,2,4-triazol-1-yl)-propanenitrile	WIF: 00-02 C.
37	2-cyclohexyloxy-2-(2-fluorophenyl)-	$n_D^{20}:1.5300$
-	3-(imidazol-1-yl)-propanenitrile	ng .1.5500
38	2-cyclohexyloxy-2-(2-fluorophenyl)-	MP: 80-82° C.
	3-(1,2,4-triazol-1-yl)-propanenitrile	
39	2-cyclopentyloxy-2-(2-fluorophenyl)-	MP: 165-168° C. (D)
	3-(imidazol-1-yl)-propanenitrile,	
	hydronitrate	
40	2-cyclohexyloxy-2-(2-fluorophenyl)-	MP: 205-206° C. (D)
	3-(imidazol-1-yl)-propanenitrile,	~~ \
	hydronitrate	
41	2-cyclopentyloxy-2-(2-methylphenyl)-	MP: 78-81° C.
	3-(1,2,4-triazol-1-yl)-propanenitrile	

The azolyl propanenitriles according to the present invention, as well as their acid addition salts, are nearly colorless and odorless oils or solids. The salts are 60 slightly soluble in water but soluble in polar organic solvents such as acetonitrile, N,N-dimethylformamide, lower alcohols, chloroform and methylene chloride. The free bases dissolve poorly in water and more or less well in organic solvents such as, for example, alcohols, 65 ethers or chlorinated hydrocarbons.

(D) = Decomposition

The starting materials, are 3-aryl-respectively 3-alkylsulfonyloxy-propanenitriles of the general formula

II, with X representing aryl-respectively alkylsulfonyloxy have not previously been described in the literature. They are obtained by hydroxymethylating in known manner, already known phenyl acetonitriles of the general formula

wherein R and R₁ have the above-given meanings, to obtain 3-hydroxypropanenitrile of the general formula

which are reacted with suitable sulfonic acid derivatives, such as, for example, sulfonic acid chloride, if necessary with the addition of an acid binder. The hydroxy methyl compounds of general formula IV were not previously disclosed in the literature. The phenylacetonitrile of the general formula III are obtained by reaction of O-sulfonated cyanohydrine with the corresponding alcohol R₁OH.

The following examples serve to illustrate various utilities for the compounds according to the present invention.

The actual concentration of the active substances used is given in ppm (parts per million of spray liquid). The fungicidal activity is calculated in the following Examples from infection data determined in each instance, as follows:

$$100 - \frac{\text{Infection in treated} \cdot 100}{\text{Infection in untreated}} = \% \text{ Activity}$$

Example 42

Effect of Prophylactic Leaf Treatment Against Real Mildew Erysiphe graminis on Barley in a Greenhouse.

Young barley plants in the stage of the first leaves are sprayed dripping wet with the given concentrations. After drying of the spray coating, the treated plants as well as untreated control plants are innoculated with dry mildew spores by stroking the test plants with infected plants. Thereafter the test plants are cultivated in a greenhouse at about 20°-22° C., and one week later the percentage of infection on the leaf surfaces is determined. The excellent activities of the compounds according to the present invention are evident from the following test data:

)		% Activity Against Erysiphe graminis with Active Substance Concentration						
	Compound	250	25	2.5	ppm			
•	2-cyclopentyloxy-3-(imidazol-1-yl)-2-(2-methylphenyl)-propanenitrile, hydronitrate	100	100	100				
,	2-cyclopentyloxy-2-(2-methyl-phenyl)-3-(1,2,4-triazol-1-yl)-propanenitrile, hydronitrate	100	100	98				
	2-cyclohexyloxy-3-(imidazol-1-	100	100	100				

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	gr	Against aminis v	ctivity Erysiph with Act Concenti	tive	5		gra	Against <i>minis</i> v	ctivity Erysiph vith Act oncentr	ive
Compound	250	25	2.5	ppm	_	Compound	250	25	2.5	ppm
yl)-2-(2-methylphenyl)-propane- nitrile, hydronitrate 2-cyclohexyloxy-2-(2-methyl-	100	100	>90			2-cyclohexyloxy-2-(2,4-dichloro- phenyl)-3-(1,2,4-triazol-1-yl)- propanenitrile, hydronitrate	98	94	92	
phenyl)-3-(1,2,4-triazol-1-yl)- propanenitrile, hydronitrate					10	2-(4-chlorophenyl)-2-cyclopentyl- oxy-3-(imidazol-1-yl)-propanenitrile	100	100	100	
2-cyclohexyloxy-3-(imidazol-1- yl)-2-(2-methylphenyl)-propane- nitrile	100	100	100			2-(4-chlorophenyl)-2-cyclopentyl- oxy-3-(imidazol-1-yl)-propane- nitrile, hydronitrate	100	100	100	
2-cyclohexyloxy-2-(2-methyl- phenyl)-3-(1,2,4-triazol-1-yl)- propanenitrile	100	100	>90		15	2-(4-chlorophenyl)-2-cyclopentyl- oxy-3-(1,2,4-triazol-1-yl)-propane- nitrile	100	100	100	
2-cyclopetyloxy-3-(imidazol-1- yl)-2-(2-methylphenyl)-propane- nitrile	100	100	100			2-(4-chlorophenyl)-2-cyclopentyl- oxy-3-(1,2,4-triazol-1-yl)- propanenitrile, hydronitrate	100	100	100	
2-cyclopentyloxy-2-(2-methylphenyl)-3-(1,2,4-triazol-1-yl)-propanenirile	100	100	100		•	propulation, any dronterate	*************************************		· · · · · · · · · · · · · · · · · · ·	:
2-cyclohexyloxy-3-(imidazol-1- yl)-2-phenyl-propanenitrile	100	100	100		20	The composition according to as a 10% or 20% formulation				
2-cyclohexyloxy-3-(imidazol-1- yl)-2-phenyl-propanenitrile, hydro- nitrate	100	100	100			Example	_			
2-(2-chlorophenyl)-2-cyclohexyl- oxy-3-(imidazol-1-yl)-propanenitrile	100	100	95		25	Effect of Prophylactic L Erysiphe Cichoracearum with	eaf T	reatm	ent A	gainst
2-(2-chlorophenyl)-2-cyclohexyl- oxy-3-(imidazol-1-yl)-propane- nitrile, hydronitrate	100	100	100			Greenhouse. Pumpkin plants sprayed drip				
2-cyclohexyloxy-2-phenyl-3- (1,2,4-triazol-1-yl)-propanenitrile	100	100	87			active substance concentration means of dusting with dry mi	ons ar	e inn	oculat	ed by
2-cyclohexyloxy-2-phenyl-3- (1,2,4-triazol-1-yl)-propanenitrile, hydronitrate	100	100	100		30	cichoracearum, after drying of then incubated in a greenhouse	the sp	ray c	oating	s, and
2-(4-chlorophenyl)-2-cyclohexyl- oxy-3-(imidazol-1-yl)-propane- nitrile, hydronitrate	100	100	100			innoculated but untreated co- week, the infected leaf surface		_		
2-(2-chlorophenyl)-2-cyclohexyl- oxy-3-(1,2,4-triazol-1-yl)-propane- nitrile	100	100	100	•	35	age of the total leafe surface. The designation "S" in the fungicidal activity is also acco				
2-(2-chlorophenyl)-2-cyclohexyl- oxy-3-(1,2,4-triazol-1-yl)-propane- nitrile, hydronitrate	100	100	100			the plants (after the treatment mined. That is, the active sul	and i	s posi	tively	deter-
2-cyclopentyloxy-3-(imidazol-1-yl)- 2-phenyl-propannitrile	100	100	95		40	systematically into the growth there to, provide 100% activit	n area v agair	of the	plant ldew.	s, and
2-cyclopentyloxy-3-(imidazol-1-yl)- 2-phenyl-propanenitrile, hydro- nitrate	100	100	100					<u></u>		
2-(2-chlorophenyl)-2-cyclopentyl- oxy-3-(imidazol-1-yl)-propanenitrile	100	100	100		45	Compounds	E	rysiphe (vity Aga cichorac ive subs	earum
2-(2-chlorophenyl)-2-cyclopentyl- oxy-3-(imidazol-1-yl)-propane-	100	100	100		43	According to the Invention		conc	entratio 0.5	
nitrile, hydronitrate 2-cyclopentyloxy-2-phenyl-3- (1,2,4-triazol-1-yl)-propanenitrile	100	100	100			2-cyclopentyloxy-3-(imidazol- 1-yl)-2-(2-methylphenyl)-pro-	10		100	r.
2-cyclopentyloxy-2-phenyl-3- (1,2,4-triazol-1-yl)-propane- nitrile, hydronitrate	100	100	100		50	panenitrile, hydronitrate 2-cyclopentyloxy-2-(2-methyl-	10)Os	100s	
2-(2-chlorophenyl)-2-cyclopentyl- oxy-3-(1,2,4-triazol-1-yl)-propane-	100	100	87			phenyl)-3-(1,2,4-triazol-1-yl)- propanenitrile, hydronitrate 2-cyclohexyloxy-3-(imidazol-1-	10	0 0s	100	-
nitrile 2-(2-chlorophenyl)-2-cyclopentyl- oxy-3-(1,2,4-triazol-1-yl)-propane-	100	100	-		55	yl)-2-(2-methylphenyl)-propane- nitrile, hydronitrate 2-cyclohexyloxy-2-(2-methyl-	10)Os	100s	
nitrile, hydronitrate 2-cyclohexyloxy-2-(2,4-dichloro- phenyl)-3-(imidazol-1-yl)-	100	100	87			phenyl)-3-(1,2,4-trizol-1-yl)- propanenitrile, hydronitrate 2-cyclohexyloxy-3-(imidazol-1-	10	10s	100	
propanenitrile 2-cyclohexyloxy-2-(2,4-dichloro- phenyl)-3-(imidazol-1-yl)-	100	100	88		60	yl)-2-(2-methylphenyl)-propane- nitrile 2-cyclohexyloxy-2-(2-methyl-	10)O s	100s	
propanenitrile, hydronitrate 2-(4-chlorophenyl)-2-cyclohexyl- oxy-3-(1,2,4-triazol-1-yl)-	100	100	100		_ -	phenyl)-3-(1,2,4-triazol-1-yl)- propanenitrile 2-cyclopentyleoxy-3-(imidazol-1-			100s	
propanenitrile 2-(4-chlorophenyl)-2-cyclohexyl- oxy-3-(1,2,4-triazol-1-yl)-	100	100	94			yl)-2-(2-methylphenyl)-propane- nitrile 2-cyclopentyloxy-2-(2-methylphenyl)-			100s 100s	
propanenitrile, hydronitrate 2-cyclohexyloxy-2-(2,4-dichloro-	100	100	100		65	3-(1,2,4-triazol-1-yl)-propane- nitrile				
phenyl)-3-(1,2,4-triazol-1-yl)- propanenitrile						2-cyclohexyloxy-3-(imidazol-1- yl)-2-phenyl-propanenitrile	10	0 0s	100s	

-continued

Compounds According to	Erysipi with a	ctivity A he cichora active sul ancentrat	ostance	5	Compounds According to		Erysiph with a	ctivity A e cichora ctive sub ncentrati	stance
the Invention	5	0.5	ppm	-	the Invention		5	0.5	
2-cyclohexyloxy-3-(imidazol-1-	100s	100	Pro-	-					ppm
yl)-2-phenyl-propanenitrile,	1003	100			nitrile, hydronitrate Comparison agent		20	Δ	nnm
hydronitrate					2-(1-methyl-n-heptyl)-4,6-		99.5	98.5	_ ppm
2-(2-chlorophenyl)-2-cyclo-	100	100		10	dinitrophenol-crotonate		77.5	76.5	
hexyloxy-3-(imidazol-1-yl)- propanenitrile					· · · · · · · · · · · · · · · · · · ·				, , , , , , , , , , , , , , , , , , ,
2-(2-chlorophenyl)-2-cyclo-	100	100			The comments of the same of th		20~	•	• .•
hexyloxy-3-(imidazol-1-yl)-	100	100			The compositions are prov	naea :	as 20%	tormi	ulations
propanenitrile, hydronitrate					dispersible in water.				
2-cyclohexyloxy-2-phenyl-3-	100	100		15	Exam	nle 44			
(1,2,4-triazol-1-yl)-propane- nitrile				15		•			
2-(2-chlorophenyl)-2-cyclo-	100	100			Effect of Prophylactic				
hexyloxy-3-(1,2,4-triazol-1-	100	100			Rust Puccinia Hordei with B	arley i	in a Clin	matized	i Plant
yl)-propanenitrile					Growth Chamber.				
2-(2-chlorophenyl)-2-cyclo-	100	100		20	Young barley plants in the	e stage	of the	first lea	ives are
hexyloxy-3-(1,2,4-triazol-1-				20	sprayed wet with the given	conce	entratio	ns. Aft	er dry-
yl)-propanenitrile, hydronitrate 2-cyclopentyloxy-3-(imidazol-1-	100	100			ing of the spray coatings, the	he trea	ated pla	nts as	well as
yl)-2-phenyl-propanenitrile	100	100			untreated control plants ar		_		
2-cyclopentyloxy-3-(imidazol-1-	100	100			stroking over with dwarf ru			•	
yl)-2-phenyl-propanenitrile,				<u></u>	plants are then placed in a	olant-e	rowth	chamb	er. The
hydronitrate 2 (2 oblorphorul) 2 ovolo	***	400		25	plants are there cultivated for	r a nei	riod of	ten dav	s at 15°
2-(2-chlorphenyl)-2-cyclo- pentyloxy-3-(imidazol-1-yl)-	100	100			C., during the first two days	_		•	
propanenitrile					saturated air atmosphere is p				
2-(2-chlorophenyl)-2-cyclo-	100	97			portion of rust-infected leaf				
pentyloxy-3-(imidazol-1-yl)-					portion of rust-infected leaf	Surrac	ic is est	шасси	•
propanenitrile, hydronitrate	4.00			30	<u> </u>				
2-cyclopentyloxy-2-phenyl-3- (1,2,4-triazol-1-yl)-propane-	100	100				% A	ctivity A	gainst P	uccinia
nitrile					Compounds		ei with ac	_	
2-cyclopentyloxy-2-phenyl-3-	100	100			According		Conce	ntration	
(1,2,4-triazol-1-yl)-propane-					to the Invention	500	250	25	ppm
nitrile, hydronitrate				35	2-cyclopentyloxy-3-(imidazol-	100	100	>90	
2-(2-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol-1-	97	95			1-yl)-2-(2-methylphenyl)-pro-				
yl)-propanenitrile					panenitrile, hydronitrate	100	00		
2-(2-chlorophenyl)-2-cyclo-	100	100			2-cyclopentyloxy-2-(2-methyl-phenyl)-3-(1,2,4-triazol-1-	100	98		
pentyloxy-3-(1,2,4-triazol-1-					yl)-propanenitrile, hydronitrate				
yl)-propanenitrile, hydronitrate				40	2-cyclohexyloxy-3-(imidazol-1-	100	>90		
2-cyclohexyloxy-2-(2,4-dichloro- phenyl)-3-(imidazol-1-yl)-propane-	100	100			yl)-2-(2-methyphenyl)-propane-				
nitrile					nitrile, hydronitrate	100			
2-cyclohexyloxy-2-(2,4-dichloro-	100	98			2-cyclohexyloxy-2-(2-methyl-phenyl)-2-(1,2,4-triazol-1-yl)-	100		_	
phenyl)-3-(imidazol-1-yl)-propane-					propanenitrile, hydronitrate				
nitrile, hydronitrate				45	2-cyclohexyloxy-3-(imidazol-1-	100	_	_	
2-(4-chlorophenyl)-2-cyclohexyl- oxy-3-(1,2,4-triazol-1-yl)-propane-	100	100		45	yl)-2-(2-methylphenyl)-pro-				
nitrile					panenitrile				
2-(4-chlorophenyl)-2-cyclohexyloxy-	100	100			2-cyclohexylox-2-(2-methyl-phenyl)-3-(1,2,4-triazol-1-	100	_	_	
3-(1,2,4-triazol-1-yl)-propane-					yl)-propanenitrile				
nitrile, hydronitrate	* -			EO	2-cyclopentyloxy-3-(imidazol-1-	100	100		
2-cyclohexyloxy-2-(2,4-dichloro-	100	100		50	yl)-2-(2-methylphenyl)-propane-				
phenyl)-3-(1,2,4-triazol-1-yl)- propanenitrile					nitrile	**~	4.0-		
2-cyclohexyloxy-2-(2,4-dichloro-	100	96			2-cyclopentyloxy-2-(2-methyl-phenyl)-3-(1,2,4-triazol-1-	100	100	-	
phenyl)-3-(1,2,4-triazol-1-yl)-		- -			yl)-propanenitrile				
propanenitrile, hydronitrate	_ =	-		- -	2-cyclohexyloxy-3-(imidazol-1-	100	100		
2-(4-chlorophenyl)-2-cyclopentyl-	100	100		55	yl)-2-phenyl-propanenitrile	-	-		
oxy-3-(imidazol-1-yl)-propane- nitrile					2-cyclohexyloxy-3-(imidazol-1-		95		
2-(4-chlorophenyl)-2-cyclopentyl-	100	100			yl)-2-phenyl-propanenitrile, hydronitrate				
oxy-3-(imidazol-1-yl)-propane-					2-(2-chlorophenyl)-2-cyclo-	100	100		
nitrile, hydronitrate		_			hexyloxy-3-(imidazol-1-yl)-	100	100		
2-(4-chlorophenyl)-2-cyclopentyl-	100s	100		6 0	propanenitrile				
oxy-3-(1,2,4-triazol-1-yl)-propane- nitrile					2-(2-chlorophenyl)-2-cyclo-	_	98		
2-(4-chlorophenyl)-2-cyclopentyl-	100s	100			hexyloxy-3-(imidazol-1-yl)- propanenitrile, hydronitrate				
oxy-3-(1,2,4-triazol-1-yl)-propane-		200			2-cyclohexyloxy-2-phenyl-3-	_	98		
nitrile, hydronitrate					(1,2,4-triazol-1-yl)-propane-		70		
2-cyclohexyloxy-2-phenyl-3-(1,2,4-	100	100		65	nitrile				
triazol-1-yl)-propanenitrile hydro- nitrate					2-cyclohexyloxy-2-phenyl-3-	100	100	-	
					(1,2,4-triazol-1-yl)-propane-				
	100	100							
2-(4-chlorophenyl)-2-cyclohexyl- oxy-3-(imidazol-1-yl)-propane-	100	100			nitrile, hydronitrate 2-(4-chlorophenyl)-2-cyclo-	100	100	90	

-continued

Compounds According	% Activity Against Puccinia hordei with active Substance Concentration					
to the Invention	500	250	25	ppm		
hexyloxy-3-(imidazol-1-yl)-pro-		<u> </u>				
panenitrile, hydronitrate						
2-(2-chlorophenyl)-2-cyclo-	_	95				
hexyloxy-3-(1,2,4-triazol-1-yl)-propanenitrile, hydronitrate						
2-cyclopentyloxy-3-(imidazol-	100	100	90			
1-yl)-2-phenyl-propanenitrile			, ,			
2-cyclopentyloxy-3-(imidazol-	100	100				
1-yl)-2-phenyl-propanenitrile,						
hydronitrate 2-(2-chlorophenyl)-2-cyclo-		05	0.2			
pentyloxy-3-(imidazol-1-yl)-	_	95	93			
propanenitrile		•				
2-(2-chlorophenyl)-2-cyclo-	100	100	85			
pentyloxy-3-(imidazol-1-yl)-						
propanenitrile, hydronitrate	100	100	.05			
2-cyclopentyloxy-2-phenyl- 3-(1,2,4-triazol-1-yl)-	100	100	95			
propanenitrile						
2-cyclopentyloxy-2-phenyl-	·	95	_			
3-(1,2,4-triazol-1-yl)-pro-						
panenitrile, hydronitrate	44-					
2-(2-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol-	100	100	85			
l-yl)-propanenitrile						
2-cyclohexyloxy-2-(2,4-	100	100	85			
dichlorophenyl)-3-(imidazol-						
1-yl)-propanenitrile						
2-cyclohexyloxy-2-(2,4-	100	100	_			
dichlorophenyl)-3-(imidazol- 1-yl)-propanenitrile, hydro-						
nitrate						
2-(4-chlorophenyl)-2-cyclo-	100	100	_			
hexyloxy-3-(1,2,4-triazol-1-						
yl)-propanenitrile	100					
2-(4-chlorophenyl)-2-cyclo- hexyloxy-3-(1,2,4-triazol-1-	100	100	95			
yl)-propanenitrile, hydro						
nitrate						
2-cyclohexyloxy-2-(2,4-	100	100	_			
dichlorophenyl)-3-(1,2,4-				•		
triazol-1-yl)-propanenitrile		0.5				
2-cyclohexyloxy-2-(2,4-dichlorophenyl)-3-(1,2,4-	_	95				
triazol-1-yl)-propane-						
nitrile, hydronitrate						
2-(4-chlorophenyl)-2-cyclo-	100	100	100			
pentyloxy-3-(imidazol-1-						
yl)-propanenitrile 2-(4-chlorophenyl)-2-cyclo-	100	100	100			
pentyloxy-3-(imidazol-1-	100	100	100			
yl)-propanenitrile, hydronitrate						
2-(4-chlorophenyl)-2-cyclo-	100	100	100	•		
pentyloxy-3-(1,2,4-triazol-			-			
1-yl)-propanenitrile	100	100	100			
2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol-	100	100	100			
1-yl)-propanenitrile, hydro-						
nitrate						
Comparison Agent						
2,3-dihydro-5-carbox-		97.5	<75			
anilido-6-methyl-1,4-						
oxathiine-4,4-dioxide						

The compositions are provided at 10% or 20% formulations dispersible in water.

Example 45

Effect of Prophylactic Leaf Treatment Against the Leaf-Spot Disease Cerospora Beticola in Sugar Beets (Beta Vulgaris).

Sugar beet plants with four well developed leaf flakes are sprayed so as to become dripping wet with the given concentrations. After drying of the spray coatings, the treated plants as well as untreated control plants are uniformly sprayed with a suspension of 15,000 cerocospora spores per ml. At 26° C. and under water vapor-saturated air, the plants are incubated four days in a greenhouse. Thereafter, at a temperature of about 22° C. they are kept an additional ten days in a greenhouse. The portion of infected leaf surface is estimated.

O Compounds According	% Activity against Cercosporal beticola with Active Substance Concentration				
to the Invention	500	100	ppm		
2-cyclohexyloxy-3-(imidazol- 1-yl)-2-phenyl-propanenitrile	100	<u> </u>			
2-cyclohexyloxy-3-(imidazol- 1-yl)-2-phenyl-propanenitrile hydronitrate	99	93			
2-(2-chlorophenyl)-2-cyclo- hexyloxy-3-(imidazol-1-yl)- propanenitrile	93				
2-(2-chlorophenyl)-2-cyclo- hexyloxy-3-(imidazol-1-yl)- propanenitrile, hydronitrate	97	86			
2-cyclohexyloxy-2-phenyl-3- (1,2,4-triazol-1-yl)-propane- nitrile	100	90			
2-cyclohexyloxy-2-phenyl-3- (1,2,4-triazol-1-yl)-propane- nitrile, hydronitrate	100	100			
2-(2-chlorophenyl)-2-cyclo- hexyloxy-3-(1,2,4-triazol- 1-yl)-propanenitrile	100	83			
2-(2-chlorophenyl)-2-cyclo- hexyloxy-3-(1,2,4-triazol- 1-yl)-propanenitrile, hydro- nitrate	100				
2-cyclopentyloxy-3-(imidazol- 1-yl)-2-phenyl-propanenitrile	100	99			
2-cyclopentyloxy-3-(imidazol- 1-yl)-2-phenyl-propanenitrile hydronitrate	100	96			
2-(2-chlorophenyl)-2-cyclo- pentyloxy-3-(imidazol-1- yl)-propanenitrile, hydronitrate	100	99			
2-cyclopentyloxy-2-phenyl- 3-(1,2,4-triazol-1-yl)- propanenitrile	100	100			
2-cyclopentyloxy-2-phenyl- 3-(1,2,4-triazol-1-yl)- propanenitrile, hydronitrate	100	100			
2-(2-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol-1- yl)-propanenitrile	100	100			
2-(2-chlorophenyl)-2-cyclo- pentyleoxy-3-(1,2,4-triazol- 1-yl)-propanenitrile, hydro- nitrate	100	100	•		
2-cyclohexyloxy-2-(2,4- dichlorophenyl)-3-(imidazol- 1-yl)-propanenitrile	99	93			
2-cyclohexyloxy-2-(2,4- dichlorophenyl)-3-(imidazol- l-yl)-propanenitrile, hydro- nitrate	93	80			
2-(4-chlorophenyl)-2-cyclo- hexyloxy-3-(1,2,4-triazol- 1-yl)-propanentrile	100	84			
2-(4-chlorophenyl)-2-cyclo- hexyloxy-3-(1,2,4-triazol- 1-yl)-propanenitrile, hydro-	100	82			
2-cyclohexyloxy-2-(2,4-dichlorophenyl)-3-(1,2,4-	100	_			
2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(imidazol-1-	100	96			
dichlorophenyl)-3-(1,2,4- triazol-1-yl)-propanenitrile 2-(4-chlorophenyl)-2-cyclo-		 96 100			

peopanenitrile, hydronitrate

2-(4-chlorophenyl)-2-cyclo-

100

100

Compounds According	% Activity against Cercosporal beticola with Active Substance Concentration				
to the Invention	500	100 ppr			
pentyloxy-3-(1,2,4-triazol- 1-yl)-propanenitrile 2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol- 1-yl)-propanenitrile, hydro- nitrate	100	96			
The compounds are provided as 10 persible in water.	% or 20% :	formulation	s dis-		
2-(2-chlorophenyl)-2-cyclopentyl- oxy-3-(imidazol-1-yl)-propane- nitrile	100	99			

Example 46

Effect of Prophylactic Spray Treatment Against Fusarium Colmorum in Club Millet (Setaria Italica).

Young millet plants of three to four cm height are sprayed dripping wet with the given concentrations. After drying of the spray coatings, the treated plants as well as untreated control plants are sprayed with a 30% biomalt-containing aqueous suspension of fusarium 25 spores (800,000 per ml), and then incubated moist in a greenhouse at 20°-22° C. After six days, the percent portion of infected leaf surface is estimated.

Compounds According	% Activity against Fusarium culmorum with Active Substan Concentration		
to the Invention	500	ppm	
2-cyclopentyloxy-3-(imidazol- 1-yl)-2-(2-methylphenyl)- propanenitrile, hydronitrate	97		
2-cylcopentyloxy-2-(2-methyl- phenyl)-3-(1,2,4-triazon-1-	97		
yl)-propanenitrile, hydronitrate 2-cyclohexyloxy-3-(imidazol-1- yl)-2-(2-methylphenyl)-propane-	96		
nitrile, hydronitrate 2-cyclohexyloxy-2-(2-methyl- phenyl)-3-(1,2,4-triazol-1-	91		
yl)-propanenitrile, hydronitrate 2-cyclohexyloxy-3-(imidazol-1- yl)-2-(2-methylphenyl)-	97		
propanenitrile 2-cyclohexyloxy-2-(2-methyl- phenyl)-3-(1,2,4-triazol-1-	96		
yl)-propanenitrile 2-cyclopentylxoy-3-(imidazol- 1-yl)-2-(2-methylphenyl)-	99		
propanenitrile 2-cyclopentyloxy-2-(methyl- phenyl)-3-(1,2,4-triazol-1-	. 97		
yl)-propanenitrile 2-cyclopentyloxy-3-(imidazol- 1-yl)-2-phenyl-propanenitrile	95		
2-cyclopentyloxy-3-(imidazol- l-yl)-2-phenyl-propanenitrile, hydronitrate	90		
2-(2-chlorophenyl)-2-cyclo- pentyloxy-3-(imidazol-1-yl)-	90		
propanenitrile 2-(2-chlorophenyl)-2-cyclo- pentyloxy-3-(imidazol-1-yl)-	93		
oropanenitrile, hydronitrate 2-(4-chlorophenyl)-2-cyclo- bentyloxy-3-(imidazol-1-yl)-	97		
propanenitrile 2-(4-chlorophenyl)-2-cyclo- pentyl-oxy-3-(imidazol-1-yl)-	95		
propanenitrile, hydronitrate 2-(4-chlorophenyl)-2-cyclo-	90		

pentyloxy-3-(1,2,4-triazol-

-continued

	Compounds According	% Activity against Fusarium culmorum with Active Substanc Concentration				
5	to the Invention	500	ppm			
10	1-yl)-propanenitrile 2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol- 1-yl)-propanenitrile, hydro- nitrate	95				

The compounds are provided as 10% or 20% formulations dispersible in water.

Example 47

Effect of Prophylactic Spray Treatment Against Botrytis Cinerea in Tomato Plants.

Young tomato plants with at least two well developed leaf flakes are sprayed dripping wet with the given active substance concentrations. After drying of the spray coatings, the treated plants as well as untreated control plants are innoculated by means of spraying of a suspension of about one million botrytis spores per ml fruit juice solution. Subsequently the plants are incubated moist in a greenhouse at about 20° C. After crumbling of the untreated plants (=100% infection) the degree of infection of the treated plants is determined.

30	Compounds According to	% Activity Against Botrytis cinerea with Active Substance Concentration				
	the Invention	250	ppm			
35	2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(imidazol-1-yl)- propanenitrile	80				
	2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(imidazol-1-yl)- propanenitrile, hydronitrate Comparison Agent from	80				
40	DE-OS 26 04 047					
	2-(imidazol-1-yl-methyl)-2-phenyl- hexanenitrile hydronitrate	5				

Example 48

Effect of Prophylactic Spray Treatment Against Helminthosporium Teres (pyrenophora teres) in Barley.

Young barley plants in the stage of the first leaves are sprayed dripping wet with the given concentrations. After drying of the spray coatings, the treated plants as well as untreated control plants are sprayed with an aqueous conidiospore suspension (about 50,000 per ml) of Helminthosporium Teres and then incubated in a moisture-chamber in a greenhouse for a period of two days at 20°-22° C. Thereafter the plants are cultivated in a greenhouse at about 20°-22° C. One week after the innoculation, the percent portion of infected leaf surface is estimated.

60	Compounds According to	% Activity Against Helminthosporium Teres with Active Substance Concentration	
	the Invention	500	ppm
65	2-cyclopentyloxy-3- (imidazol-1-yl)-2-(2- methylphenyl-propane- nitrile, hydronitrate	80	
	2-cyclohexyloxy-3- (imidazol-1-yl)-2-	80	

Compounds According to	Teres with Ac	t Helminthosporium tive Substance	
the Invention	500	ppm	- ,
(2-methylphenyl)- propanenitrile 2-cyclohexyloxy-2-	80		
(2-methylphenyl)-3- (1,2,4-triazol-1-yl)- propanenitrile			10

Example 49

Effect of Prophylactic Spray Treatment Against Cochlliobolus Miyabeanus in Rice Plants.

Young rice plants in the stage of the start of the second leaves are sprayed dripping wet with the given concentrations. After drying of the spray coatings, the treated plants as well as untreated control plants are sprayed with an aqueous conidia suspension (about 250,000 per ml) of the fungus, and then incubated moist in a greenhouse at about 24° C. After four days the 25 percent portion of the infected leaf surface is noted.

Compound According to	% Activity Against Phytophthore infestans with Active Substance Concentration	
the Invention	500	ppm
2-cyclohexyloxy-2-phenyl- 3-(1,2,4-triazol-1-yl)- propanenitrile	91	

Example 51

Activity Against Apple Scab (Venturia inequalis), Prophylactic and Curative.

The five youngest leaves of apple shoots planted in free acreage are treated dripping wet. After drying of the spray coatings, these shoots as well as untreated shoots are sprayed with a suspension of 320,000 conidiospore of the fungus per ml 3% glucose solution in distilled water, and then confined for a period of 53 hours in polyethylene sacks under shade. Eight days after the innoculation a number of the untreated, innoculated shoots are subjected to a curative treatment (dripping wet). Five weeks after the innoculation the percent degree of scab covering on the leaf surfaces is estimated.

Compounds According to	% Activity Against Cochliobolus miyabeanus with Active Substance Concentration	
the Invention	500	ppm
2-cyclopentyloxy-3-(imidazol- 1-yl)-2-(2-methylphenyl)-	80	
propanenitrile, hydronitrate 2-cyclopentyloxy-2-(2- methylphenyl)-3-(1,2,4-triazol- 1-yl)-propanenitrile, hydro-	80	
nitrate 2-cyclohexyloxy-3-(imidazol)- 1-yl)-2-(2-methylphenyl)-	80	
propanenitrile, hydronitrate 2-cyclohexyloxy-2-(2-methyl- pehnyl)-3-(1,2,4-triazol- 1-yl)-propanenitrile, hydro-	80	•
nitrate 2-cyclohexyloxy-3-(imidazol- 1-yl)-2-(2-methylphenyl)- propanenitrile	80	
2-cyclohexyloxy-2-(2-methyl-phenyl)-3-(1,2,4-triazol-1-yl)-propanenitrile	80	
2-cyclopentyloxy-3-(imidazol- 1-yl)-2-(2-methylphenyl)- propanenitrile	80	

Example 50

Effect of Prophylactic Spray Treatment Against *Phytophthora Infestans* in Tomato Plants.

Young tomato plants with at least two well developed leaf flakes are sprayed dripping wet. After drying of the spray coatings, the treated plants as well as unctreated control plants are sprayed with an aqueous suspension of about 80,000 phytophthora sporangia per ml, the suspension having been incubated for two hours at 11° C. The plants are then incubated moist in a greenhouse at about 18° C. After five days the percent portion of infected leaf surface is estimated.

30	Compound	% Activity Against Apple Scab with Active Substance Concentration		
	According to	# CA	······································	
	the Invention	Prophylactic	Curativa	
		Trophylactic	Curative	
35	2-cyclopentyloxy-3- (imidazol-1-yl)-2-(2- methylphenyl)-propane- nitrile	100	86	
	Control (untreated)	25 <i>0</i> /_ i=fo	ation	
	Control (unitreateu)	35% infe	ction	
	Compounds	% Activity Again with Active Seconds	Substance	
40	According to			
	the Invention	Prophylactic	300 ppm Curative	
	2-cyclopentyloxy-3-(imidazol- 1-yl)-2-(2-methylphenyl)- propanenitrile	86		
45	2-cyclohexyloxy-3-(imidazol- 1-yl)-2-phenyl-propanenitrile	98		
	2-cyclohexyloxy-3-(imidazol- 1-yl)-2-phenyl-propanenitrile, hydronitrate	90		
	2-cyclopentyloxy-3-(imidazol- 1-yl)-2-phenyl-propanenitrile	97	81	
50	2-cyclopentyloxy-3-(imidazol- 1-yl)-2-phenyl-propanenitrile, hydronitrate	91	90	
	2-cyclopentyloxy-2-phenyl-3- (1,2,4-triazol-1-yl)-propane- nitrile	100	95	
55	2-cyclopentyleoxy-2-phenyl-3- (1,2,4-triazol-1-yl)-propane- nitrile, hydronitrate	100	90	
	2-(2-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol-1- yl)-propanenitrile	98	73	
6 0	2-(2-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol- 1-yl)-propanenitrile, hydronitrate	88		
	2-cychlohexy-2-(2,4-dichloro- phenyl)-3-(imidazol-1-yl)-pro- panenitrile	84		
65	2-(4-chlorophenyl)-2-cyclo- hexyloxy-3-(1,2,4-triazol-1- yl)-propaneitrile	100	93	
	2-(4-chlorophenyl)-2-cyclo- hexyloxy-3-(1,2,4-triazol-	100	99.5	

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1-yl)-propanenitrile, hydro- nitrate	•	
2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(imidazol-1- yl)-propanenitrile	96	9 9
2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(imidazol-1-yl)-	89	95
propanenitrile, hydronitrate 2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol-	99.5	94
1-yl)-propanenitrile 2-(4-chlorophenyl)-2-cyclo- pentylxoy-3-(1,2,4-triazol-1- yl)-propanenitrile, hydro- nitrate	100	99

The following operational examples serve for illustration of use possibilities of the compounds according to the present invention as growth regulators:

Example 52

Growth-regulatory Effect with Sugar Beets.

Sugar beets are treated in a pre-germination technique with a calculated 0.5 kg active substances per ha, and then further cultivated in a greenhouse. Eight days 25 after the application, the percent restraint of growth is determined as the influence of the preparation.

Compounds According to the Invention	Percent Growth Restraint	30
2-cyclohexyloxy-2-(2- methylphenyl)-3-(1,2,4-triazol- 1-yl)-propanenitrile, hydro-	40	
nitrate 2-cyclohexyloxy-2-(2-methyl- phenyl)-3-(1,2,4-triazol-1- yl)-propanenitrile	20	3:
Control	0	

The treatment of the plants leads to a growth restraint and a dark green coloration of the leaves.

Example 53

Growth Regulation with Sugar Beets and Corn. Corn and sugar beets are placed in a greenhouse after a pre-germination spraying with the substances according to the present invention. Eleven days after the treatment, growth-regulatory effects are determined by way of the percent growth restraint. 0.5 kg active substance 50 per ha led to the following results:

Compounds According to		Percent Growth Restraint	
the Invention	Corn	Sugar Beets	
2-(2-chlorophenyl)-2-cyclo- hexyloxy-3-(imidazol-1-yl)- propanenitrile	14	14	
2-(2-chlorophenyl)-2-cyclo- hexyloxy-3-(imidazol-1-yl)- propanenitrile, hydronitrate	21	14	
2-(4-chlorophenyl)-2-cyclo- hexyloxy-3-(imidazol-1-yl)- propanenitrile, hydronitrate	14	14	
2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(imidazol-1-yl)- propanenitrile	21	29	
2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol- 1-yl)-propanenitrile	36	57	

-continued	l .
	Percent Group

Compounds According to	Percent Grow Restraint	
the Invention	Corn	Sugar Beets
Control	0	0

The results show that the substances according to the present invention clearly restrain the longitudinal 10 growth of the treated plants.

Example 54

Effect of Prophylactic Leaf Treatment Against Plasmopara viticola with Grape Plants in a Greenhouse.

Young grape plants with about 5 to 8 leaves are sprayed dripping wet with 500 ppm active substance concentration. After drying of the spray coatings, the undersides of the leaves are sprayed with an aqueous deposit of sporangia of the fungus (about 55,000 per ml), and then incubated in a greenhouse at 22°-24° C. in an atmosphere as water vapor-saturated as possible.

From the second day, the air moisture is brought back to a normal level (30 to 70% saturation) for a period of 3-4 days, and then held at water vapor-saturation for 1 further day. Subsequently each leaf is evaluated insofar as the percent portion of fungus-infected surface, and the average per treatment is used for determination of the fungicidal activity as described above.

Compounds According to the Invention	Activity Against Plasmopara viticola
2-cyclopentyloxy-3-(imidazol-	89
1-yl)-2-(2-methylphenyl)-	
propaneitrile, hydronitreat	
2-cyclopentyloxy-2-(2-methyl-	84
phenyl)-3-(1,2,4-triazol-1-	
yl)-propanenitrile, hydronitrate	
2-cyclohexyloxy-3-(imidazol-1-	100
yl)-2-(2-methylphenyl)-	
propanenitrile, hydronitrate	
2-cyclohexyloxy-2-(2-methyl-	85
phenyl)-3-(1,2,4-triazol-1-	
yl)-propanenitrile, hydronitrate	
2-cyclohexyloxy-2-phenyl-3-	91
(1,2,4-triazol-1-yl)-propanenitrile	
2-cyclohexyloxy-3-	. 95
(imidazol-1-yl)-2-(2-methyl-	
phenyl)-propanenitrile	
2-cyclohexyloxy-2-(2-methyl-	91
phenyl)-3-(1,2,4-triazol-1-	
yl)-propanenitrile	
2-cyclopentyloxy-3-(imidazol-	98
1-yl)-2-(2-methylphenyl)-	
peopanenitrile	
2-cyclopentyloxy-3-(imidazol-	100
1-yl)-2-phenyl-propanenitrile	
2-cyclopentyloxy-3-(imidazol-	73
1-yl)-2-phenyl-propanenitrile,	
hydronitrate	
2-(2-chlorophenyl)-2-cyclo-	90
pentyloxy-3-(imidazol-1-yl)-	
propanenitrile	
2-(2-chlorophenyl)-2-cyclo-	97
pentyloxy-3-(imidazol-1-yl)-	
propanenitrile, hydronitrate	
2-cyclopentyloxy-2-phenyl-3-	95
(1,2,4-triazol-lyl)-propane-	
nitrile	
2-cyclopentyloxy-2-phenyl-3-	98
(1,2,4-triazol-1-yl)-propane-	F #
nitrile, hydronitrate	
2-(2-chlorophenyl)-2-cyclo-	98
pentyloxy-3-(1,2,4-triazol-1-yl)-	- -
propanenitrile	
2-(4-chlorophenyl)-2-cyclo-	99.5

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Compounds According to the Invention	Activity Against Plasmopara viticola
pentyloxy-3-(imidazol-1-yl)- propanenitrile	
2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(imidazol-1-yl)- propanenitrile, hydronitrate	100
2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol-1-yl)- poropanenitrile	97
2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol-1- yl)-propanenitrile, hydro- nitrate	85

The agents according to the invention are provided as 10% or 20% formulations dispersible in water.

Example 55

Activity in vitro Against *Mucor spec*. of Soybeans. Aqueous preparations of the active substances are mixed with sterilized, liquid agar nutrient base (2% biomalt, 2% agar) at about 45° C. in such manner that the mixture contains 250 ppm active substance. The mixture is then placed in polystyrene petri dishes of 8.5 cm diam. to a height of 5 mm. After cooling of the nutrient base, each petri dish is provided with a 5 mm diam. agar piece overgrown with Mucor. Per treatment, two dishes and also four untreated dishes are 30 inoculated.

After five days incubation at 22° C. in the dark, the colony diameters are measured and after removal of the inoculate quantity of 5 mm, employed as follows for calculation of the fungicidal activity:

Compounds According to the Invention	% Activity Against Mucor Spec.
2-cyclopentyloxy-2-(2-methyl- phenyl)-3-(1,2,4-triazol-1-yl)- propanenitrile, hydronitrate	80
2-cyclopentyloxy-3-(imidazol- 1-yl)-2-(2-methylphenyl)- propanenitrile	75
2-cyclohexyloxy-2-phenyl- 3-(1,2,4-triazol-1-yl)- propanenitrile	100
2-cyclopentyloxy-3-(imidazol- 1-yl)-2-phenyl-propanenitrile	95
2-(2-chlorophenyl)-2-cyclo- pentyloxy-3-(imidazol-1-yl)- propanenitrile	94
2-cyclopentyloxy-2-phenyl- 3-(1,2,4-triazol-1-yl)- propanenitrile	100
2-cyclopentyloxy-2-phenyl- 3-(1,2,4-triazol-1-yl)- propanenitriel, hydronitrate	75
2-(2-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol-1- yl)-propanenitrile	98
2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(imidazol-1- yl)-propanenitrile	100
yl)-propanemirhe 2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(imidazol)1- yl)-propanenitrile, hydronitrate	· 7 7
2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol-1-	100

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Compounds According to the Invention	% Activity Against Mucor Spec.
yl)-propanenitrile 2-(4-chlorophenyl)-2-cyclo- pentyloxy-3-(1,2,4-triazol-1- yl)-propanenitrile, hydronitrate Comparison agent	87
2-cyano-2-methoxyiminoacetic acid ethylaminocarbonylamide	50

The agents according to the invention are provided as 10% or 20% formulations dispersible in water.

Example 56

Effect in vitro Against *Pseudomonas phaseolicola* (Fat Spot Disease of Beans).

Aqueous preparations of the active substances are mixed with sterilized, liquid agar base (2% biomalt, 2% agar) at about 56° C. in such manner that the mixtures contain 50 ppm active substance. The mixtures are then placed in polystyrene petri dishes of 8.5 cm. diam. to a height of 5 mm. After cooling of the nutrient base, the middle of each petri dish is dabbed with a suspension of pseudomonas phaseolicola in distilled water by means of 5 mm. quantity inoculation loop. Per treatment, two dishes and four untreated dishes are inoculated. After four and one half weeks incubation at 20°-22° C. in the dark, the colony diameters are determined. After withdrawal of the inoculate quantity, the colonies are employed as follows for a calculation of bactericidal activity:

100 - Diameter without inoculate in treated · 100

Diameter without inoculate in untreated = % activity

Compounds According to the Invention	% Activity Against Pseudomonas phaseolicola
2-(2-chlorophenyl)-2-cyclo-	82
pentyloxy-3-(imidazol-1-yl)-	•
propanenitrile, hydronitrate	
2-cyclopentyloxy-2-phenyl-3-	73
(1,2,4-triazol-1-yl)-propane- nitrile	
2-cyclopentyloxy-2-phenyl-	91
3-(1,2,4-triazol-1-yl)-	
propanenitrile, hydronitrate	
2-(2-chlorophenyl)-2-cylco-	91
pentyloxy-3-(1,2,4-triazol-1-yl)-	
propanenitrile	
2-(4-chlorophenyl)-2-cyclo-	100
pentyloxy-3-(imidazol-1-	
yl)-propanenitrile	
2-(4-chlorophenyl)-2-cyclo-	100
pentyloxy-3-(imidazol-1-yl)-	
propanenitrile, hydronitrate	
2-(4-chlorophenyl)-2-cyclo-	91
pentyloxy-3-(1,2,4-triazol-1-	
yl)-propanenitrile	
2-(4-chlorophenyl)-2-cyclo-	91
pentyloxy-3-(1,2,4-triazol-1-	
yl)-propanenitrile, hydronitrate	
Comparison Agent	
2-cyano-2-methoxyiminoacetic	0
acid-ethylaminocarbonylamide	•

The agents according to the invention are provided as 10% or 20% formulations dispersible in water.

It will be understood that each of the elements described above, or two or more together, will also find a useful application in other types of biocidal preparation differing from the types described above.

While the invention has been illustrated and described as embodied in azolyl-propanenitriles, processes for the production of these compounds as well as biocidal compositions containing the same, it is not intended to be limited to the details shown, since various modifications and structural changes may be made without departing in any way from the spirit of the present invention.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can, by applying current knowledge, can readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic and specific aspects of this invention.

What is desired to be protected by Letters Patent is set forth in the appended claims.

We claim:

1. Azolyl-propanenitrile of the formula

$$\begin{array}{c|c}
C & Y & \\
R - C - CH_2 - N & \\
C & N
\end{array}$$

in which

R is phenyl, methylphenyl, fluorophenyl, chlorophenyl or dichlorophenyl,

R₁ is cyclopentyl or cyclohexyl, and

Y is N or CH, or a salt thereof with nitric acid.

2. The compound according to claim 1 wherein R is 2-fluorophenyl, 3-fluorophenyl, 4-fluorophenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 2,4-dichlorophenyl, 3,4-dichlorophenyl, 2,6-dichlorophe-40

nyl, 2-methylphenyl, 3-methylphenyl, or 4-methylphenyl, nyl,

R₁ is cyclopentyl or cyclohexyl, and Y is N or CH.

- 3. The compound according to claim 1, 2-cyclopen-tyloxy-3-(imidazol-1-yl)-2-(2-methylphenyl)-propanenitrile, hydronitrate.
- 4. The compound according to claim 1, 2-cyclopen-tyloxy-3-(imidazol-1-yl)-2-phenyl-propanenitrile, hy10 dronitrate.
 - 5. The compound according to claim 1, 2-cyclopentyloxy-2-phenyl-3-(1,2,4-triazol-1-yl)-propanenitrile, hydronitrate.
- 6. The compound according to claim 1, 2-(2-chlorophenyl)-2-cyclopentyloxy-3-(1,2,4-triazol-1-yl)-propanenitrile, hydronitrate.
- 7. The compound according to claim 1, 2-(4-chlorophenyl)-2-cyclopentyloxy-3-(imidazol-1-yl)-propanenitrile, hydronitrate.
- 8. The compound according to claim 1, 2-(4-chlorophenyl)-2-cyclopentyloxy-3-(1,2,4-triazol-1-yl)-propanenitrile, hydronitrate.
- 9. A fungicidal, plant growth regulating and bactericidal composition comprising from 10 to 90 percent by weight of at least one compound according to claim 1 in mixture with a carrier material, with or without an adjuvant.
- 10. Method or protecting plants against fungi, comprising applying onto or within the locus of said plants a fungicidally-effective amount of the composition according to claim 9.
- 11. Method of regulating the growth of plants, comprising applying onto or within the locus of said plants a growth-regulatory-effective amount of the composition according to claim 9.
 - 12. Method of protecting plants against bacteria, comprising applying onto or within the locus of said plants a bactericidally-effective amount of the composition according to claim 9.

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